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(21) International Application Number: PCT/GB96/03216 (22) International Filing Date: 23 December 1996 (23.12.96) (30) Priority Data: 9601685.2 27 January 1996 (27.01.96) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): TAYLOR, John, Anthony [GB/GB]; 20 Branksome Avenue, Prestwich, Manchester M25 1AG (GB). (74) Agents: MAYALL, John; Zeneca Specialties, Intellectual Property Group, Hexagon House, P.O. Box 42, Blackley, Manchester M9 8ZS (GB) et al.		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DYES CONTAINING A 2,4,5-TRIFLUORO-3,6-DICYANOPHENYL REACTIVE GROUP AND USE THEREOF (57) Abstract Dyes having at least one 2,4,5-trifluoro-3,6-dicyanophenyl group and their use in the coloration of substrates, particularly cellulosic textile materials.		

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DYES CONTAINING 2,4,5-TRIFLUORO-3,6-DICYANOPHENYL REACTIVE GROUP AND USE THEREOF

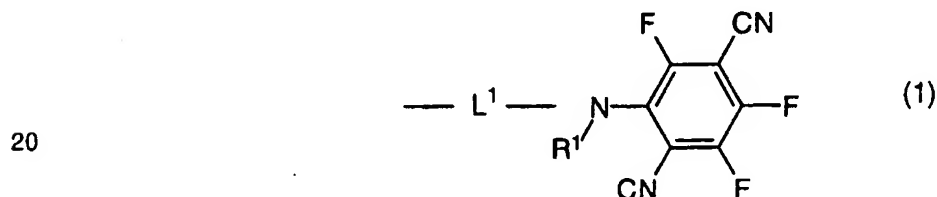
This invention relates to dyes having a 2,4,5-trifluoro-3,6-dicyanophenyl reactive group (hereinafter a TFDC group), to a process for their manufacture, to a process for the coloration of materials using the dyes and to materials when coloured by the dyes.

5 According to the present invention there is provided a dye having at least one 2,4,5-trifluoro-3,6-dicyanophenyl group.

It is preferred that the TFDC group is attached to an amine group in the dye, more preferably an amine group of formula -NR¹- wherein R¹ is H or alkyl, especially H or C₁₋₄-alkyl. The amine group is preferably attached to a carbon atom in an aromatic ring, for example a phenylene or naphthylene ring.

Preferably the dye is water-soluble. Preferred dyes according to the invention contain at least two, more preferably at least 3 and preferably less than 11 sulpho groups.

15 One class of dye according to the invention contains a group of the Formula (1):



wherein:

L¹ is an arylene group; and
R¹ is as hereinbefore defined.

25 In addition to the TFDC group the dye may contain a further reactive group, for example a pyrimidinyl amino group, a vinyl sulphone group or a triazinylamino reactive group.

The pyrimidinylamino reactive group is preferably halopyrimidinylamino, especially trichloropyrimidinylamino, and more especially a difluorochloropyrimidinylamino group.

30 The term vinyl sulphone group includes vinyl sulphonyl and groups which are convertible to vinyl sulphonyl in the presence of aqueous alkali, for example -CH₂CH₂OSO₃H and -CH₂CH₂SSO₃H.

The triazinylamino reactive group is preferably a 2,4,6-s-triazinylamino group carrying a labile atom or group and either an alkoxy group, especially C₁₋₄-alkoxy, or an optionally substituted alkylamino group, especially optionally substituted phenylamino or optionally substituted alkylamino. Preferred optional
5 substituents are selected from sulpho and DFDC. The preferred optionally substituted alkylamino group is an optionally substituted C₁₋₄-alkylamino group, for example CH₃-NH- and CH₃CH₂-NH-.

By a labile atom or group it is meant an atom or group which is bound by a chemical bond to the triazine nucleus, which atom or group is displaceable by a
10 hydroxyl group of cellulose under mildly alkaline aqueous conditions to form a covalent bond between the triazine nucleus and cellulose. As examples of such atoms or groups there may be mentioned halogen atoms such as F and Cl; sulphonic acid groups; thiocyno groups; quaternary ammonium groups such as trialkylammonium groups; and optionally substituted pyridinium groups such as 3- and 4-carboxy pyridinium groups.

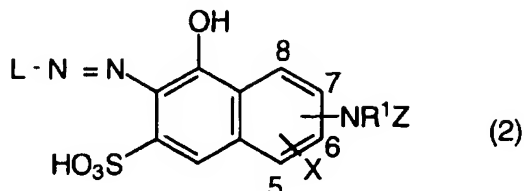
The water-soluble dye according to the invention is preferably a water-soluble azo, anthraquinone, phthalocyanine, triphenodioxazine or formazan dye. Thus preferred dyes of the present invention are of the formula D-(NR¹-Z)_n wherein Z is 2,4,5-trifluoro-3,6-dicyanophenyl, n is 1, 2 or 3, D is the residue of an azo, anthraquinone, phthalocyanine, triphenodioxazine or formazan chromophore and R¹ is as hereinbefore
20 defined. Examples of groups represented by D are given in the following pages in Formulae (2) to (9) wherein D is the portion of the illustrated molecules other than group -NR¹Z.

Preferred water-soluble azo dyes are monoazo and disazo dyes.

Preferred monoazo dyes are formula L-N=N-L¹-NR¹-Z wherein L is an aryl
25 or heteroaryl group, L¹ is an arylene group and Z and R¹ are as hereinbefore defined.

It is preferred that each aryl or arylene group independently is a mono- or di-cyclic aryl or arylene group. Preferred aryl groups are optionally substituted phenyl and naphthyl, and preferred arylene groups are optionally substituted phenylene and optionally substituted naphthylene. Preferred heteroaryl groups are pyridinyl and
30 pyrazolonyl.

A first preferred monoazo dye is of the Formula (2) or salt thereof:



wherein:

X is H or sulphy; and

10 L, R¹ and Z are as hereinbefore defined.

L is preferably optionally substituted phenyl or naphthyl, especially a phenyl or naphthyl group having at least one sulphy substituent. Further optional substituents which may be present on L include a halogen atom, especially chlorine; an alkyl radical, especially C₁₋₄-alkyl, more especially methyl; an acylamino radical, especially
15 acetylamino, benzamido or sulphonylated benzamido; amino; hydroxy; and an alkoxy radical, especially C₁₋₄-alkoxy, more especially methoxy.

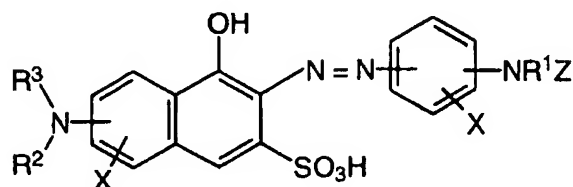
As examples of phenyl groups having at least one sulphy substituent there may be mentioned 2-, 3- or 4-sulphophenyl; 2-sulpho-4-nitrophenyl; 2-sulpho-5-nitrophenyl; 4-sulpho-2-methylphenyl;
20 5-sulpho-2-methylphenyl; 2-sulpho-4-methylphenyl; 5-sulpho-2-methoxyphenyl; 2-sulpho-4-methoxyphenyl; 4-sulpho-2-chlorophenyl; 5-sulpho-2-carboxyphenyl; 2,4-disulphophenyl; 2,5-disulphophenyl; and 3,5-disulphophenyl.

As examples of naphthyl groups having at least one sulphy substituent
25 there may be mentioned 1-sulphonaphth-2-yl; 1,5,7-trisulphonaphth-2-yl; 3,6,8-trisulphonaphth-2-yl; 5,7-disulphonaphth-2-yl; 6-sulphonaphth-2-yl; 4-, 5-, 6-, or 7-sulphonaphth-1-yl; 4,8-disulphonaphth-1-yl; 3,8-disulphonaphth-1-yl; 2,5,7-trisulphonaphth-1-yl; and 3,5,7-trisulphonaphth-1-yl.

30 Preferred optional substituents which may be present on L¹ are those mentioned above for L.

In dyes of Formula (2) -NR¹Z is preferably at the 6-, 7- or 8-position, especially the 6- or 8- position. When -NR¹Z is at the 8-position, it is preferred that X is a sulphy group at the 5- or 6- position.

A second preferred monoazo dye is of the Formula (3) or a salt thereof:



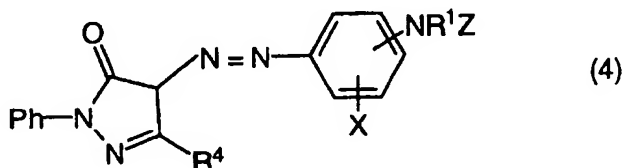
(3)

wherein:

R^3 is H or C_{1-4} -alkyl;
 R^2 is H, C_{1-4} -alkyl; C_{1-4} -alkanoyl; optionally substituted benzoyl, especially benzoyl or sulphobenzoyl, acetyl, propanoyl, Δ -butanoyl or isobutanoyl; and

Z, R^1 and each X is as hereinbefore defined.

A third preferred monoazo dye is of the Formula (4) or salt thereof:



(4)

wherein:

Ph is an optionally substituted phenyl group, especially sulphophenyl;
 R^4 is CN, CH_3 or carboxy; and
 R^1 , X and Z are as hereinbefore defined.

A preferred disazo dye is of Formula (5) or salt thereof:



wherein:

A and B are each independently optionally substituted phenylene or naphthylene;
 and

R^1 , L and Z are as hereinbefore defined.

It is preferred that B is optionally substituted naphthylene and A is optionally substituted phenylene. The optional substituents which may be present on A or B are preferably independently selected from halo, especially chloro; alkoxy, especially C_{1-4} -alkoxy; alkyl, especially methyl; sulpho; carboxy; hydroxy; amino; acylamino especially as acetamido, benzamido and sulphonated benzamido, and

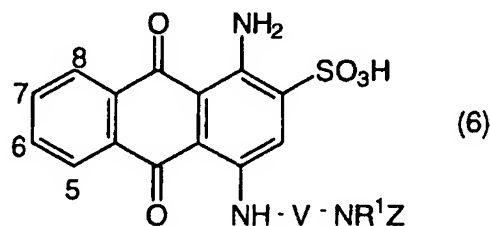
pyrimidinylamino or triazinylamino cellulose-reactive groups.

As Examples of groups represented by A and B there may be mentioned phenylene, sulphophenylene, ureidophenylene, 7-sulpho-1, 4-naphthylene, 6-sulpho-1,4-naphthylene and 8-sulpho-1,4-naphthylene.

5

A preferred anthraquinone dye is of the Formula (6) or a salt thereof:

10



15

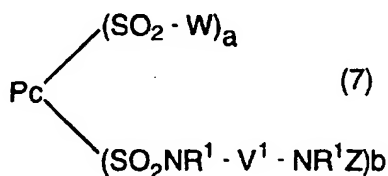
wherein the anthraquinone nucleus optionally contains a sulphonic acid group in the 5-, 6-, 7-, or 8-position; V is a divalent organic linking group, preferably of the benzene series; and R¹ and Z are as hereinbefore defined.

V is preferably phenylene, diphenylene, or 4,4'-divalent stilbene or azobenzene radicals which are optionally sulphonated. It is preferred that V contains one sulphonic acid group for each benzene ring present therein.

20

A preferred phthalocyanine dye is of the Formula (7) or a salt thereof:

25

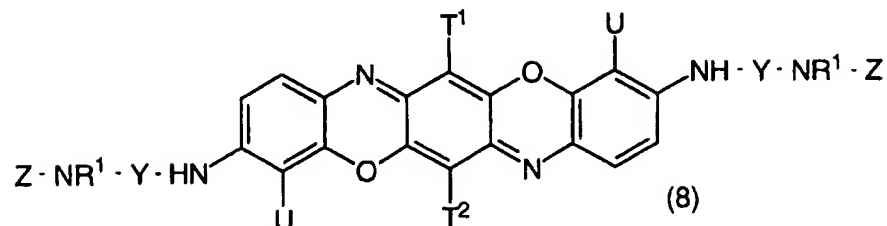


30

wherein Pc is a metallo-phthalocyanine nucleus, preferably copper or nickel phthalocyanine; each R¹ and Z is as hereinbefore defined; each W independently is a hydroxy or a substituted or unsubstituted group, V¹ is a divalent organic linking group, preferably a C₁₋₄-alkylene or phenylene linking group; and a and b are each independently 1, 2 or 3 provided that a + b is not greater than 4.

35

A preferred triphenodioxazine dye is of the Formula (8) or a salt thereof :



wherein :

10 each Y independently is a covalent bond, C₂₋₄-alkylene, phenylene or sulphophenylene;

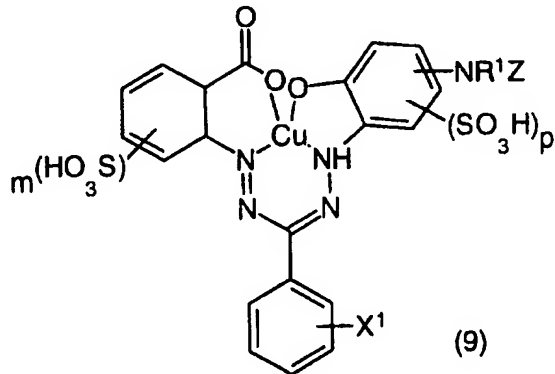
U is H or SO₃H;

T¹ and T² are halo, especially chloro, C₁₋₄-alkyl, or C₁₋₄-alkoxy; and

each Z and R¹ independently is as hereinbefore defined.

15 Each Y is preferably -C₂H₄- or -C₃H₆-, U is preferably SO₃H, and T¹ and T² are preferably Cl, methyl or ethyl.

A preferred formazan dye is of the Formula (9) or a salt thereof :



wherein :

X¹ is H, SO₃H or Cl;

30 m and p each independently have a value of 0, 1 or 2; and

Z and R¹ as hereinbefore defined;

provided that the formazan group has at least one, and preferably at least two, sulpho groups.

It is preferred that m and p each have a value of 1.

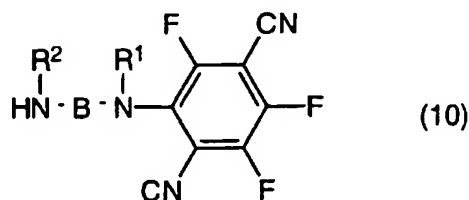
35 Dyes according to the invention may be prepared by a process comprising condensation of 1,2,4,5-tetrafluoro-3,6-dicyanobenzene and a dye having a nucleophilic

group, especially a $-NR^1H$ group, preferably in a liquid medium. It is preferred that the condensation is performed at 10-90°C, especially 20-90°C, more especially 40-90°C. The liquid medium is preferably an aqueous medium or comprises dimethylsulphoxide.

The condensation is preferably performed in the presence of an acid-binding agent. The function of the acid-binding agent is to neutralise hydrogen fluoride as it is formed during the condensation. Accordingly any acid-binding agent may be used provided that it is not present in such a concentration that it causes hydrolysis of the reactants or causes some other side-reaction. It is preferred to use an alkali metal hydroxide, carbonate or bicarbonate, added at such a rate that the pH of the mixture stays within the range of 5.0 to 6.0.

According to a further aspect of the present invention there is provided a compound of the Formula (10) and use thereof for the preparation of a dye :

15



wherein :

20

R^1 , R^2 and B are as hereinbefore defined.

In a compound of Formula (10) B is preferably C_{2-4} -alkylene, optionally substituted phenylene, more preferably optionally substituted phen-1,3-ylene, wherein the optional substituents are as hereinbefore described for B.

25

A compound of Formula (10) wherein R^2 is H and B is an optionally substituted phenylene or naphthylene group is useful as a diazotisable amine which may be coupled with a coupling component to give an azo dye. Diazotisation may be achieved by treating a solution of the compound of Formula (10) with sodium nitrite and hydrochloric acid at below 5°C.

30

A compound of Formula (10) may be prepared by condensing 1,2,4,5-tetrafluoro-3,6-dicyanobenzene with diamine of formula $HN(R^2)-B-NH(R^1)$, preferably in dimethylsulphoxide at 20-90°C, wherein R^1 , R^2 and B are as hereinbefore defined.

Although dye formulae have been shown in the form of their free acid in this specification, the invention also relates to the dyes in the salt form, particularly their salts with alkali metals such as the sodium, lithium or mixed sodium/lithium salt.

35

The present invention also provides a process for the coloration of a substrate comprising applying thereto a dye according to the present invention,

preferably in aqueous solution.

The reactive dyes of the present invention are suitable for colouring natural and artificial textile materials containing amino or hydroxyl groups, for example textile materials such as wool, silk, polyamides and modified polyacrylonitrile fibres, and more especially cotton, viscose rayon and other regenerated cellulosic materials. For this purpose the dyes can be applied to the textile materials by exhaust dyeing, or by padding or by printing using printing pastes containing the conventional thickening agents or oil-in-water emulsions, whereby the textile materials are coloured bright shades and possess good fastness to light and to wet treatments such as washing and also possess good wash off.

The new dyes are particularly valuable for colouring cellulosic textile materials. For this purpose the dyes are preferably applied to the cellulosic textile material in conjunction with a treatment with an acid-binding agent, for example, sodium bicarbonate, sodium carbonate, sodium metasilicate, trisodium phosphate or sodium hydroxide, which may be applied to the cellulose textile material before, during and after the application of the dye.

The new dyes can be applied to textile materials containing amine groups, such as wool and polyamide textile materials, from a mildly alkaline, neutral or acid dyebath. The dyeing process can be carried out at a constant or substantially constant pH, that is to say the pH of the dyebath remains constant or substantially constant during the dyeing process, or if desired the pH of the dyebath can be altered at any stage of the dyeing process.

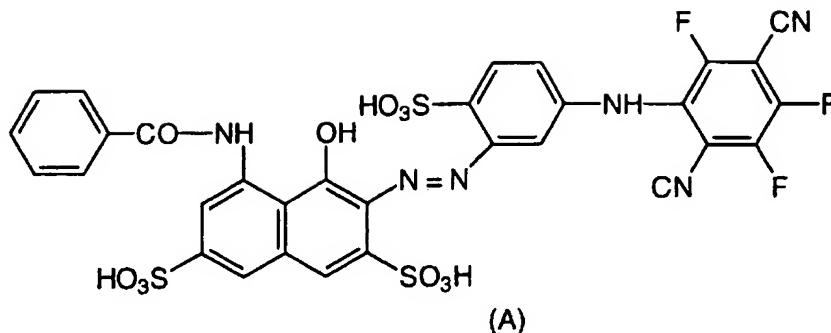
In the preferred aspect of the present invention the new dyes are applied to a textile material by printing.

The invention also provides textile materials coloured using a dye according to the invention.

The invention is illustrated but not limited by the following Examples in which all parts and percentages are by weight unless stated otherwise.

Example 1

Preparation of

Stage a

To a mixture of N-(β -hydroxyethyl)diethylamine (5.86g) and 2,4-diaminobenzene sulphonic acid (7.52g) in dimethylsulphoxide (45ml) was added 1,2,4,5-tetrafluoro-3,6-dicyanobenzene (8.25g) portionwise with stirring. The mixture was heated at 75°C for 4 hours then poured into ice/water (140 ml) to give a solution of 2-amino-4-(2,4,5-trifluoro-3,6-dicyanophenylamino)benzene sulphonic acid.

Stage b

2N NaNO₂ (27.2ml) was added to a cold solution of 2-amino-4-(2,4,5-trifluoro-3,6-dicyanophenylamino)benzene sulphonic acid in water (about 400ml) containing conc. hydrochloric acid (15ml). The mixture was stirred at <5°C for 1.5 hrs then excess nitrous acid was destroyed by adding a few drops of 10% sulphamic acid solution to give a diazo compound.

Stage c

The product of stage b was added to a solution of 1-benzoylamino-8-hydroxynaphthalene-1,3-disulphonic acid (0.05 M) at <5°C. The pH was adjusted to 6 and the mixture stirred overnight at pH 6.5/<5°C. The mixture was filtered, brine (10% w.v) added to the stirred filtrate and the resultant precipitate was collected and desalinated using Visking tubing.

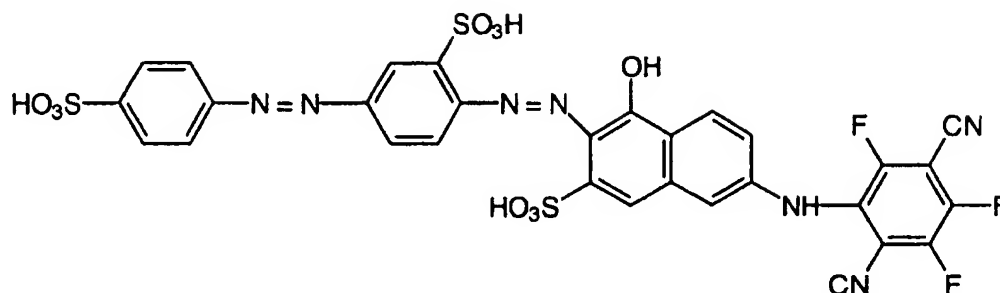
Water was evaporated from the resultant solution to give a small volume of liquid and the title product was precipitated by the addition of methylated spirits. 14.2g title product was obtained having a λ_{max} at 530nm.

Dyeing

The title product was applied to cotton by printing and found to have excellent build up and fastness.

5 Example 2

Preparation of

Stage a

1-hydroxy-6-(2,5-dicyano-3,4,6-trifluorophenyl)amino naphthalene-3-sulphonic acid was prepared by condensing tetrafluoro terephthalonitrile with 1-hydroxy-6-aminonaphthalene-3-sulphonic acid in dimethylsulphoxide.

Stage b

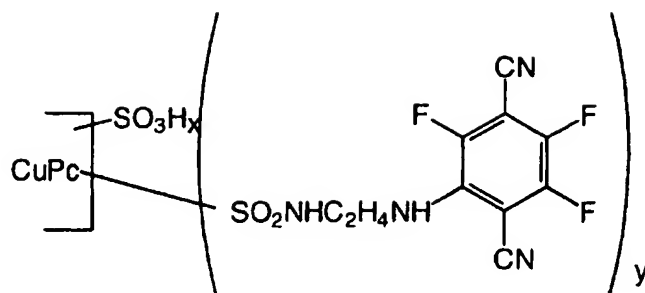
A solution of 2-sulpho-4-(4-sulphophenylazo)benzene diazonium chloride (prepared by diazotising 4-amino-3,4'-disulphoazobenzene) (0.1M) was added at <5°C to a solution of 1-hydroxy-6-(2,5-dicyano-3,4,6-trifluorophenyl)amino naphthalene-3-sulphonic acid (0.1M) in water. The mixture was stirred at pH 5, 0°C for 16 hours, allowed to warm to room temperature and filtered. Brine (10% w/v) was added to the stirred filtrate and the resultant precipitate was dissolved in the minimum quantity of water and brine (29% w/v) was added. The resultant precipitate was collected and dried to give the title product (14.6g, M.I. 1050) having a λ_{\max} at 511nm.

Dyeing

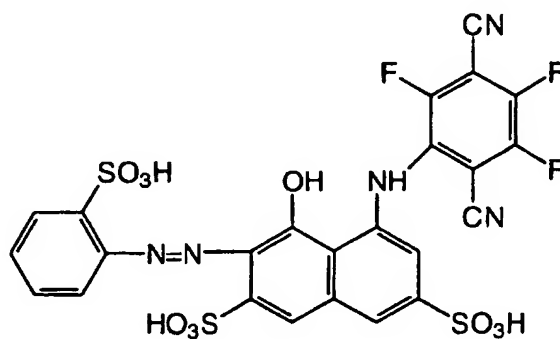
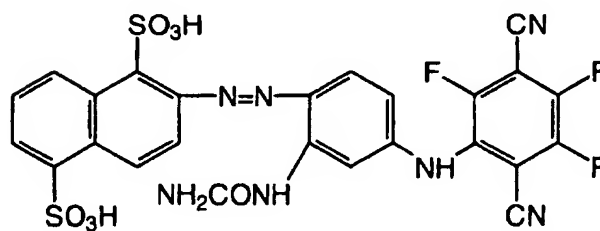
The title product was applied to cotton by exhaust dyeing and was found to have excellent build up and fastness.

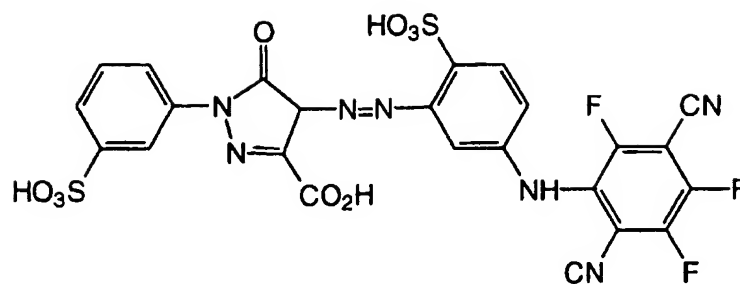
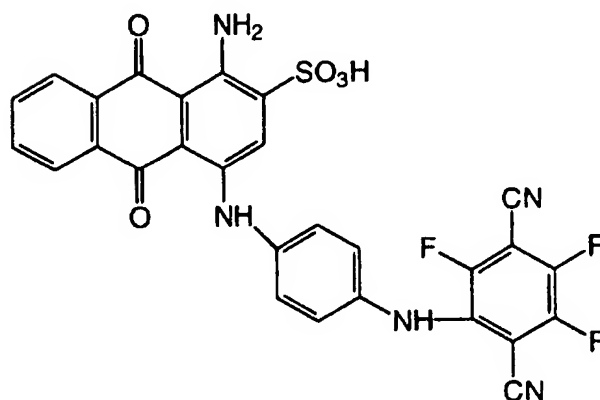
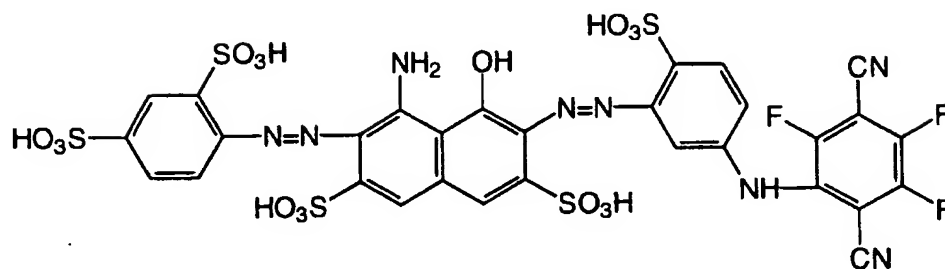
25 Examples 3 to 8

Following similar methods to those described in Examples 1 and 2 the following dyes may also be prepared:

Example 3

10 wherein CuPc is copper phthalocyanine,
 $x + y = 4$ and each of x and y independently is ≥ 1 .

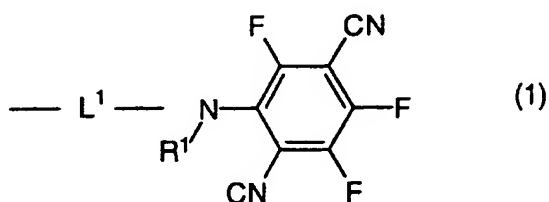
Example 4Example 5

Example 6Example 7Example 8Example 9

The method of Example 1 was repeated except that in place of 1-benzoylamino-8-hydroxynaphthalene-1,3-disulphonic acid there was used 1-amino-2-(2,5-disulphophenyl azo)-8-hydroxynaphthalene-3,6-disulphonic acid.

CLAIMS

1. A dye having at least one 2,4,5-trifluoro-3,6-dicyanophenyl group.
2. A dye according to claim 1 wherein the 2,4,5-trifluoro-3,6-dicyanophenyl group is attached to an amine group in the dye.
3. A dye according to any one of the preceding claims containing a group of the Formula (1):



wherein:

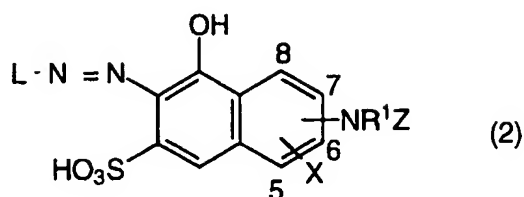
L^1 is an
arylene group; and

R^1 is H or alkyl.

4. A dye according to any one of the preceding claims of the formula $\text{D-(NR}^1\text{-Z)}_n$ wherein Z is 2,4,5-trifluoro-3,6-dicyanophenyl; n is 1, 2 or 3; D is the residue of an azo, anthraquinone, phthalocyanine, triphenodioxazine or formazan chromophore; and R^1 is H or alkyl.

5. A water-soluble dye according to claim 4 wherein D is the residue of an azo chromophore selected from monoazo and disazo chromophores.

6. A monoazo dye according to claim 1 of the Formula (2) or salt thereof:



10 wherein :

X is H or sulpho;

L is an aryl or heteroaryl group;

R¹ is H or alkyl; and

Z is 2,4,5-trifluoro-3,6-dicyanophenyl.

7. A disazo dye according to claim 1 of the Formula (5) or salt thereof:



wherein:

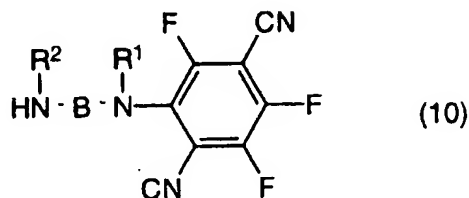
20 A and B are each independently optionally substituted phenylene or naphthylene;

L is an aryl or heteroaryl group;

R¹ is H or alkyl; and

Z is 2,4,5-trifluoro-3,6-dicyanophenyl.

8. A compound of the Formula (10):



wherein:

R¹ is H or C₁₋₄-alkyl;

R² is H, C₁₋₄-alkyl, C₁₋₄-alkanoyl or optionally substituted benzoyl; and

B is optionally substituted phenylene or naphthylene.

9. A process for the coloration of a substrate comprising applying thereto a dye according to any one of claims 1 to 7.

5 10. A process according to claim 9 wherein the substrate is a cellulosic textile material.

INTERNATIONAL SEARCH REPORT

International Application No

PLI/GB 96/03216

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09B62/78 C07C255/58

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 020 679 A (ICI LTD) 21 November 1979 see claims; examples	1-10
A	EP 0 415 585 A (ICI PLC) 6 March 1991 see column 4, line 50 - line 52; claim 4; example 3	1,8

☐ Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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